

Capacity failure on cycling or storage of lithium-ion batteries with Li–Mn–O ternary phases having spinel-framework structure and its possible solution

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Abstract

Instability of Li–Mn–O ternary phases having a spinel-framework structure especially at temperatures above 50°C is a problem in designing lithium-ion batteries with these materials. This paper describes the solubility of manganese ions from these materials in 1 M LiPF₆EC/DMC (2/1 by volume), X-ray diffraction (XRD) analysis of these materials after solubility tests, and cycle tests of lithium cells with these materials at room temperature or at temperature higher than 50°C. Severe damage was observed in both solubility and cycle tests when Li–Mn–O ternary phases were operated or stored at temperatures higher than 50°C. The XRD examinations indicated that the spinel-framework structure changed in its line shape and location. In order to cope with this problem, we intensively examined the addition of transition metal elements into Li–Mn–O phases and found possible solution on this problem. One of the possible materials is Li[Cr_{0.1}Mn_{1.9}]O₄ (Fd3m) which shows excellent performance on cycling and storage at 50°C. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium-ion batteries; Manganese oxides; Capacity failure; Storage

1. Introduction

Lithium insertion materials [1,2], such as LiCoO₂, LiNiO₂, LiCo_xNi_{1-x}O₂ (0 < x < 1), LiMn₂O₄ [3,4], and so forth, have attracted attention among battery researchers since lithium-ion batteries with LiCoO₂ and non-graphitized carbon [5] were fabricated and applied to power sources for wireless telephones, lap-top computers, and other electronic devices. Of these, Li–Mn–O ternary phases having a spinel-framework structure [3,4,6–9] are the most attractive material mainly because of materials' economy and less toxicity compared to other materials. Lithium-ion cells with Li[Li_xMn_{2-x}]O₄, where x is close to zero, show rechargeable capacity of about 120 mA h g⁻¹ and good cyclability if the materials were properly prepared and the cells were operated under continuous charge and discharge at constant current at room temperature (typically ca. 25°C). The freshly fabricated cells, however, deteriorate during storage at higher temperatures than 50°C, and consequently, cell capacities fade quickly during continuous charge and discharge at elevated temperatures

[10–13]. In order to cope with this problem, we examined capacity failure due to the solubility of manganese ions in LiPF₆-based electrolyte.

This paper describes the results on solubility tests of several lithium manganese oxide samples with or without another transition metal element (Cr, Co, Fe, or Ni) [14,15] in LiPF₆-based electrolyte, X-ray diffraction (XRD) examination before or after the solubility tests, and cycle tests of these materials in lithium cells both at room temperature and 50°C, and the possible solution of this problem is presented.

2. Experimental

The samples (LiMn₂O₄, Li[Li_xMn_{2-x}]O₄, Li[M_xMn_{2-x}]O₄; M = transition metal element) were prepared by reacting a mixture of EMD (Tosoh Hyuga) and Li₂CO₃ with or without third elements, such as Cr₂O₃, Co(NO₃)₂ · 6H₂O, Ni(NO₃)₂ · 6H₂O, Fe(NO₃)₃ · 9H₂O. Prepared samples were characterized by XRD and chemical analysis.

In measuring the solubility of manganese ions from these materials, 3 g of the each sample were put into

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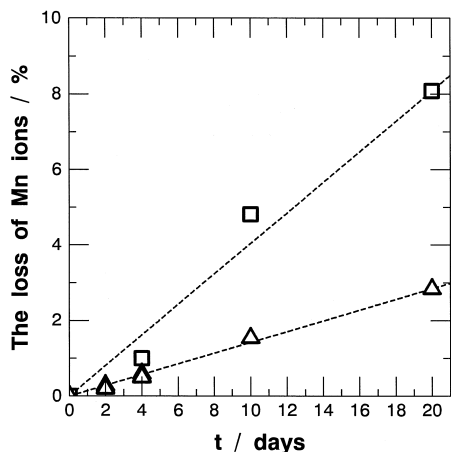


Fig. 1. The loss of manganese ions for the stoichiometric sample of $\text{Li}[\text{Li}_{0.01}\text{Mn}_{1.99}]\text{O}_4$ (open squares) and $\text{Li}[\text{Li}_{0.06}\text{Mn}_{1.94}]\text{O}_4$ (open triangles) due to the dissolution of manganese ions in 1 M LiPF_6 EC/DMC (2/1 by volume) during the storage of manganese sample in the electrolyte at 85°C for prolonged period. The loss of manganese ions in mole percents was calculated from the analytical values in moles of dissolved manganese ions and the total mole of manganese ions in the starting sample.

perfluoroalkoxy (PFA) polymer container and soaked in 15 ml of 1 M LiPF_6 EC/DMC (2/1 by volume) solution in a PFA container at room temperature, 60°C, or 85°C. Then the residual sample was separated using 0.1 μm polytetrafluoroethylene (PTFE) filter. The amount of manganese ions dissolved in the electrolyte from the sample was determined by ICP-AES. The residual sample was rinsed with DMC, and dried at 60°C. The sample was characterized by XRD and chemical analysis.

Charge and discharge tests were carried out using test cells consisting of the sample and lithium metal at room temperature or 50°C.

3. Results and discussion

All samples prepared in this study were identified as single phase having a spinel-framework structure (Fd3m) by XRD, and the BET-surface areas were about $2 \text{ m}^2 \text{ g}^{-1}$ for all samples. In this paper, $\text{Li}[\text{Li}_{0.01}\text{Mn}_{1.99}]\text{O}_4$ (Mn wt.% = 60.5; MnO_2 wt.% = 73.7; Li wt.% = 3.9; x in $\text{MnO}_x = 1.77$) is called a stoichiometric LiMn_2O_4 sample.

When the lithium cells with the stoichiometric sample were continuously cycled in voltage between 3.5 and 4.5 V at room temperature, no remarkable loss of capacity was observed even after 50 cycles. Rechargeable capacity was observed to be 125 mA h g^{-1} out of 144 mA h g^{-1} of theoretical capacity as will be shown later. However, if the cells were operated at 50°C, rechargeable capacities faded down to 90 mA h g^{-1} after 50 cycles. Electrolyte used was 1 M LiPF_6 dissolved in EC/DMC (2/1 by volume). Capacity fading is mainly due to the dissolution of manganese ions in the electrolyte from the stoichiometric

sample. Fig. 1 shows the results on the solubility tests of stoichiometric sample and $\text{Li}[\text{Li}_{0.06}\text{Mn}_{1.94}]\text{O}_4$ at 85°C. In Fig. 1, manganese ions detected in solution were given in atomic percents based on the manganese samples. As can be seen in Fig. 1, dissolution of manganese ions is a first-order reaction, suggesting that a rate-determining step is the diffusion of manganese ions or a first-order chemical reaction. The rate of loss in manganese ions from $\text{Li}[\text{Li}_{0.06}\text{Mn}_{1.94}]\text{O}_4$ is about three times slower than that of the stoichiometric sample. This is consistent with such observation that the increasing lithium content in $\text{Li}[\text{Li}_x\text{Mn}_{2-x}]\text{O}_4$ improves cyclability [7,8] as compared with stoichiometric one even at elevated temperatures. However, the rate of capacity fading at 50–60°C is critical for practical application. In order to solve this problem, several trials have been done and a possible solution to this problem has been found.

Fig. 2 shows the effect of substitution of another transition metal ions for manganese ions at the 16(d) sites. In drawing the figure, we selected the samples which showed superior effect to that of $\text{Li}[\text{Li}_x\text{Mn}_{2-x}]\text{O}_4$. The value in vertical axis corresponding to the loss of manganese ions in the sample is normalized to that for the stoichiometric sample, so that the value is comparable with each other. Increasing the lithium content in $\text{Li}[\text{Li}_x\text{Mn}_{2-x}]\text{O}_4$ gives a beneficial effect at $0 < x < 0.06$ in $\text{Li}[\text{Li}_x\text{Mn}_{2-x}]\text{O}_4$, but it levels off at $x = 0.06$. The effect of the substitution on the suppression of the loss of manganese ions due to the dissolution is in the following order; $\text{Li} < \text{Co} < \text{Fe} < \text{Ni} < \text{Cr}$. Other electrolytes, such as 1 M LiPF_6 EC/DMC (1/1 by volume), 1 M LiPF_6 EC/DMC (1/2 by volume), and 1 M LiPF_6 PC/DEC (1/4 by volume) were also examined, but the above order was unchanged. Since the chromium samples gave the best results among the samples exam-

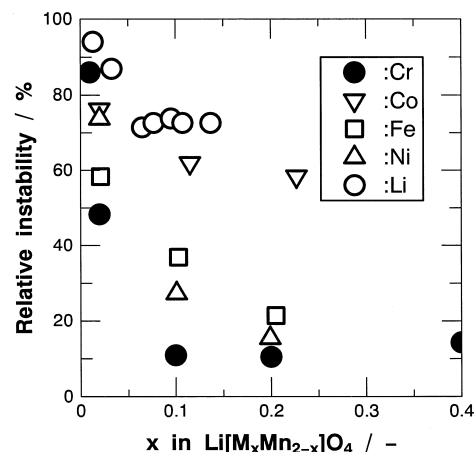


Fig. 2. The relative instability of $\text{Li}[\text{M}_x\text{Mn}_{2-x}]\text{O}_4$ (M = Cr, Co, Fe, Ni, or Li) against the stoichiometric sample of $\text{Li}[\text{Li}_{0.01}\text{Mn}_{1.99}]\text{O}_4$ during the storage in 1 M LiPF_6 EC/DMC (2/1 by volume) at 85°C for 4 days. The relative instability in percent was calculated from the loss of manganese ions in mole percents for the samples divided by that for the stoichiometric sample, i.e., the values are normalized to that of $\text{Li}[\text{Li}_{0.01}\text{Mn}_{1.99}]\text{O}_4$.

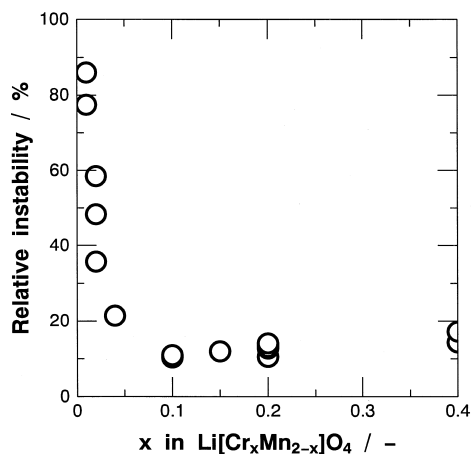


Fig. 3. The effect of chromium content x in $\text{Li}[\text{Cr}_x\text{Mn}_{2-x}]\text{O}_4$ on the relative instability against the stoichiometric sample of $\text{Li}[\text{Li}_{0.01}\text{Mn}_{1.99}]\text{O}_4$ during the storage in 1 M LiPF_6 EC/DMC (2/1 by volume) at 85°C for 4 days.

ined, the solubility tests of manganese ions were carried out in details in order to determine the optimum concentration of chromium ions in $\text{Li}[\text{Cr}_x\text{Mn}_{2-x}]\text{O}_4$. Results are shown in Fig. 3. Small addition of chromium ions gives remarkable effect on the suppression of the loss of manganese ions in a solid matrix in the region of $0 < x < 0.05$ in $\text{Li}[\text{Cr}_x\text{Mn}_{2-x}]\text{O}_4$. However, the greater increase in chromium content than $x = 0.1$ in $\text{Li}[\text{Cr}_x\text{Mn}_{2-x}]\text{O}_4$ gave no effect on the suppression. This is a good indication because the addition of chromium ions as $\text{Li}[\text{Cr}_x\text{Mn}_{2-x}]\text{O}_4$ reduces the rechargeable capacity of the lithium cell operated in voltages between 3.5 and 4.5 V. In producing positive electrode materials for lithium-ion batteries in an industrial scale, we need a margin of error in composition for the reliable supply of the material with accessible rechargeable capacity. Therefore, we have decided to conclude that $\text{Li}[\text{Cr}_{0.1}\text{Mn}_{1.9}]\text{O}_4$ is an optimum composition for the lithium-ion application.

Fig. 4 shows the XRD examinations of $\text{Li}[\text{Cr}_{0.1}\text{Mn}_{1.9}]\text{O}_4$ before and after its storage in 1 M LiPF_6 EC/DME (2/1 by volume) at 85°C for 4 days. The data obtained for the stoichiometric sample of $\text{Li}[\text{Li}_{0.01}\text{Mn}_{1.99}]\text{O}_4$ or $\text{Li}[\text{Li}_{0.06}\text{Mn}_{1.94}]\text{O}_4$ are also shown for comparison. Line broadening for every diffraction line was observed after the storage of the stoichiometric sample or $\text{Li}[\text{Li}_{0.06}\text{Mn}_{1.94}]\text{O}_4$. Although the diffracted X-ray intensity of $\text{Li}[\text{Cr}_{0.1}\text{Mn}_{1.9}]\text{O}_4$ is somewhat different between before and after the test of $\text{Li}[\text{Cr}_{0.1}\text{Mn}_{1.9}]\text{O}_4$, line broadening is hardly observed under such a severe experimental condition at 85°C . Damage of the solid matrix due to the storage of $\text{Li}[\text{Cr}_{0.1}\text{Mn}_{1.9}]\text{O}_4$ in the electrolyte at 85°C cannot be seen by XRD.

Fig. 5 shows the results on the cycle tests of lithium cells with $\text{Li}[\text{Cr}_{0.1}\text{Mn}_{1.9}]\text{O}_4$ or the stoichiometric sample of $\text{Li}[\text{Li}_{0.01}\text{Mn}_{1.99}]\text{O}_4$ operated in voltages between 3.5 and 4.5 V at room temperature or 50°C . According to our results, the stoichiometric sample gives the best perfor-

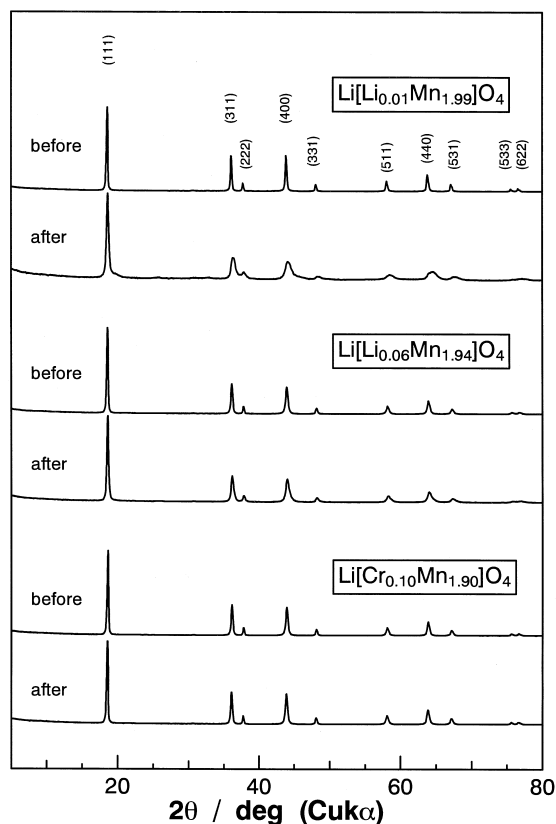


Fig. 4. Change in X-ray diffraction patterns of the samples after the storage in 1 M LiPF_6 dissolved in EC/DMC (2/1 by volume) at 85°C for 4 days.

mance in rechargeable capacity, typically 125 mA h g^{-1} , in the case of room temperature operation with constant-current continuous charge and discharge mode. However, the rechargeable capacity faded quickly cycle by cycle when the cells were operated at 50°C as seen in Fig. 5. The cell with $\text{Li}[\text{Cr}_{0.1}\text{Mn}_{1.9}]\text{O}_4$ showed smaller rechargeable capacity than that with the stoichiometric sample at room

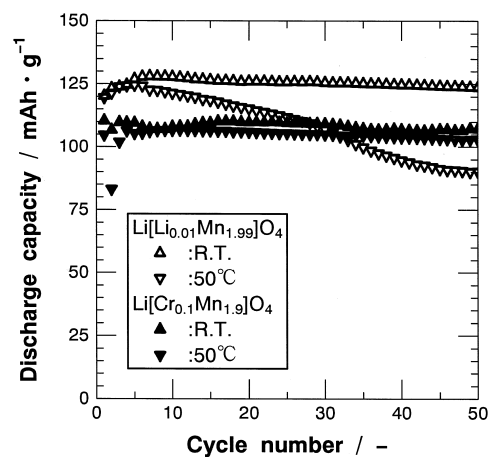


Fig. 5. Comparison of the capacity retention between lithium cells with the stoichiometric sample of $\text{Li}[\text{Li}_{0.01}\text{Mn}_{1.99}]\text{O}_4$ and $\text{Li}[\text{Cr}_{0.1}\text{Mn}_{1.9}]\text{O}_4$ operated in voltages between 3.5 and 4.5 V at a rate of 1 mA cm^{-2} at room temperature or 50°C .

temperature, but a dramatic change in rechargeable capacity was not observed even when the cell was operated at 50°C.

As were described above, $\text{Li}[\text{Cr}_{0.1}\text{Mn}_{1.9}]\text{O}_4$ is a tough material against the dissolution of manganese ions in LiPF_6 -based electrolytes, and consequently, it can be used as the positive electrodes for high-volume, long-life, practical lithium-ion batteries with the graphite-based negative electrodes [16].

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